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(54) ELECTROLYTIC CAPACITOR

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a novel electrolytic capacitor which is excellent in impedance characteristic, leakage current characteristic and reliability, and has a high breakdown voltage.

SOLUTION: The electrolytic capacitor uses an electrolyte containing a conductive polymer (A) and an organic acid onium salt (B). The electrolytic capacitor is preferably of a solid type and more preferably uses organic acid onium salt which follows. That is, the organic acid onium salt contains onium and organic acid anions; the onium cation is one or more selected from the cation group of consisting of quaternary ammonium, tertiary sulfonium, quaternary phosphonium and tertiary oxonium; and the organic acid anion one or more selected from the group of anions obtained by removing protons from organic acids of carboxylic acid, phenols, mono- or di-phosphoric acid ester and boron complex.

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* NOTICES *

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the new electrolytic capacitor using a conductive polymer (A) and organic-acid onium salt (B) in more detail about an electrolytic capacitor.
[0002]
[Description of the Prior Art] In recent years, what has an impedance low also about a capacitor in small large capacity and a RF field is called for with digitization of electronic equipment etc. Although there are a plastic film capacitor and a stacked type ceramic condenser as a capacitor for high frequency fields conventionally, by these capacitors, a configuration becomes large and large-capacity-izing is difficult. On the other hand, as a mass capacitor, there is an aluminum dry electrolytic capacitor, aluminum, or an tantalum solid electrolytic capacitor. The anode plate which consists of a valve action metal, the anodic oxide film (dielectric) formed in the anode plate front face, and the electrolyte which served both as true cathode are required for these electrolytic capacitors. For example, in the aluminum dry electrolytic capacitor, the etched anode plate and cathode aluminium foil are rolled round through a separator, and the electrolytic solution for actuation is sunk in and used for the separator.
[0003] However, there is a big problem of property degradation accompanying an electrolytic liquid spill, evaporation, etc. in an aluminum dry electrolytic capacitor. A liquefied electrolyte also has the problem that loss is large and the frequency characteristics of an impedance are remarkably inferior by ion conductivity since specific resistance is large. In order to improve these technical problems, aluminum or an tantalum solid electrolytic capacitor solidified the electrolyte. As an electrolyte of a solid electrolytic capacitor, there are conductive polymers, such as a manganic acid ghost, a 7,7,8,8-tetracyanoquinodimethane (TCNQ) salt, and polypyrrole, the poly thiophene or the poly aniline, etc.
[0004]
[Problem(s) to be Solved by the Invention] However, in the solid electrolytic capacitor using a manganic acid ghost as an electrolyte, although the technical problem about aging, such as the temperature characteristic and capacity, and loss, improves, specific resistance of a manganic acid ghost cannot say that it is high and the frequency characteristics of an impedance are enough. Breakage on a dielectric oxide film takes place by pyrolysis processing of multiple times in formation of the electrolyte which furthermore consists of a manganic acid ghost. Moreover, in the solid electrolytic capacitor which uses a TCNQ salt as an electrolyte, in case TCNQ is applied, there is a problem from which specific resistance lifting arises that an adhesive property with an anode plate foil is weak.
[0005] On the other hand by the approach of making a conductive polymer forming in a front face by the chemistry oxidation polymerization from monomers, such as a pyrrole, a thiophene, or an aniline the effect of degradation of the dielectric oxide film by the oxidizer, and formation of a conductive polymer, since there is almost no sex (defective-part restoration capacity of a dielectric oxide film) It was difficult to constitute the electrolytic capacitor with which rated voltage exceeds 35V, and when these were constituted, there was a case where buildup of the leakage current and the short circuit between anode plate-cathode occurred during aging processing and an elevated-temperature trial.

[0006] This invention solves such a technical problem and it aims at offering the electrolytic capacitor of the high withstand voltage excellent in an impedance characteristic, a leakage current property, and dependability.
[0007]
[Means for Solving the Problem] In order that this invention persons may solve the above-mentioned technical problem, as a result of inquiring wholeheartedly, the electrolytic capacitor using the electrolyte which consists of a conductive polymer (A) and organic-acid onium salt (B) found out that it could become the electrolytic capacitor excellent in an impedance characteristic, a leakage current property, and dependability with high withstand voltage. Namely, the electrolytic capacitor characterized by this invention using the electrolyte which consists of a conductive polymer (A) and organic-acid onium salt (B); they are this constituent for electrolyte formation;, and organic-acid onium salt for electrolytic capacitors.
[0008]
[Embodiment of the Invention] In this invention, a conductive polymer (A) is a compound which dopes a dopant (A-2) to a conjugated-double-bond polymer (A-1) or this polymer, and is obtained preferably. (A-1) is one sort or two sorts or more of polymerization objects of a monomer (a-1) which form a conjugated-double-bond polymer. Although it is or it dopes [whether it dopes the polymerization back (A-2) of (a-1), or] it at the time of a polymerization, (A) dopes (A-2) at the time of a polymerization [being desirable (a-1)], adds (A-2) at the time of a polymerization [being still more desirable (a-1)], and performs a polymerization at it. the time of a polymerization -- adding (A-2) -- you may be an oxidizer (a-2), and it acts also as a dopant at the same time it participates in a polymerization as an oxidizer in this case (a-2).
[0009] As ** (a-1), carbon numbers 2-30 or following compound [beyond it] (1) - (4) is mentioned.
(1) Aliphatic series system triple bond compound; acetylene, 1, 6-hepta-gene, etc.;
(2) Aromatic series conjugated compound; benzene, naphthalene, anthracene, etc.;
(3) ** hetero atom conjugated compound; non-heterocyclic compounds, such as heterocyclic compound; anilines, such as a pyrrole, a thiophene, a furan, and ethylene dioxythiophene, a sulfonation aniline, and a diphenyl sulfide.
(4) The above (1) Compound with which the alkyl groups (for example, methyl, ethyl, lauryl, a stearyl radical, etc.) of carbon numbers 1-20 of - (3), aryl groups (phenyl, naphthyl group, etc.), etc. were permuted.
These monomers (a-1) may use a kind or two sorts or more. The ** hetero atom conjugated compound of (3) is [among these] desirable, still more desirable things are a heterocyclic compound and an aniline, and especially desirable things are a pyrrole, a thiophene, ethylene dioxythiophene, and an aniline.
[0010] The compound of following (1) - (7) is mentioned as an oxidizer (a-2).
(1) transition-metals salt; -- an inorganic-acid salt (an iron sulfate, iron nitrate, ferric chloride, and perchloric acid iron --) ; organic-acid salt [oxalates (a ferrous oxalate --), such as phosphoric-acid iron, iron bromide, an iron hydroxide, a copper nitrate, a copper sulfate, and a copper chloride the aliphatic series sulfonic-acid iron (methansulfonic acid iron --) of carbon numbers 1-30, such as copper oxalate the aromatic series sulfonic-acid iron (benzenesulfonic acid iron --) of carbon numbers 7-30, such as propane sulfonic-acid iron the aliphatic series sulfonic-acid copper (methansulfonic acid copper --) of carbon numbers 1-30, such as p-toluenesulfonic-acid iron the aromatic series sulfonic-acid copper (copper benzoate --) of carbon numbers 7-30, such as propane sulfonic-acid copper], such as phthalic-acid copper; compound salts (a sodium dichromate, a potassium dichromate, an ammonium dichromate, sodium permanganate, potassium permanganate, molybdophosphoric acid sodium, etc.);
(2) Proton acid and its salt [except for the transition-metals salt of (1)]; the alkali-metal salts (sodium, potassium, etc.) of said proton acid, such as a hydrochloric acid, a sulfuric acid, a nitric acid, fluosulfonic acid, chlorosulfuric acid, a hydrofluoric acid, and the Lynn hydrofluoric acid, ammonium salt, the organic amines (trimethylamine, triethylamine, etc.) salt of carbon numbers 3-10, etc.
(3) Diazonium salt; sulfuric-acid hydrogen benzene diazonium, sulfuric-acid hydrogen o-toluene

diazonium, etc.
(4) A halogen and a halogenide; a bromine, iodine, an iodation bromine, arsenic pentafluoride, 5 antimony fluoride, silicon tetrafluoride, a phosphorus pentachloride, phosphorus pentafluoride, an aluminum chloride, aluminium bromide, etc.
(5) A peroxy acid and its salt; hydrogen-peroxide and inorganic peroxy-acids (perchloric acid, periodic acid, etc.); organic-acid-peroxide (peracetic-acid, perbenzoic acid, etc.); and the alkali-metal salts (sodium, potassium, etc.) of the above-mentioned peroxy acid, ammonium salt, the organic amines (trimethylamine, triethylamine, etc.) salt of carbon numbers 3-10, etc.
(6) Quinones; a benzoquinone, a naphthoquinone, etc.
(7) In addition, an oxidizer; sulfur trioxide, a nitrogen dioxide, ozone, etc.
A transition-metals salt, proton acid, and its salt are [among these] desirable, still more desirable things are a sulfonic-acid transition-metals salt, ferric chloride, a hydrochloric acid, and a sulfuric acid, and especially desirable things are the aliphatic series sulfonic-acid iron of carbon numbers 1-30, the aromatic series sulfonic-acid iron of carbon numbers 7-30, ferric chloride, and a sulfuric acid. In addition, (a-2) may use a kind or two sorts or more.
[0011] (A) or (A-1) -- as the approach (a-1) of forming -- being desirable (a-2) -- the following approach of (I) - (III) made to react in addition is mentioned.
(I) In the case of the approach this polymerization by the liquid phase chemistry polymerization, a capacitor element is immersed in the solution containing (a-1), and it performs an oxidation polymerization. In this case, it is desirable to add an oxidizer (a-2). In this case, a solvent may be added and viscosity and concentration may be adjusted. It is easy to be well-known as a polymerization solvent used by this polymerization. For example, water, Monoalcohol (a methanol, ethanol, propanol, isopropanol, etc.), a glycol (ethylene glycol, a diethylene glycol, and triethylene glycol --) the mono-ether (methyl cellosolve --), such as tripropylene glycol Ethylcellosolve, methyl carbitol, ethyl carbitol, butyl carbitol, The triethylene glycol monomethyl ether, the triethylene glycol monobutyl ether, Propylene glycol monomethyl ether, the propylene glycol monopropyl ether, Dipropylene glycol monomethyl ether, a tetrahydrofuran, etc., a diether (ethylene glycol wood ether and ethylene glycol diethylether --) Diethylene-glycol ethyl methyl ether, a jig lime, a TORIGU lime, Tetraethylene glycol wood ether, 1, 3-dioxane, etc., nitril (an acetonitrile, benzonitrile, etc.) and a ketone (an acetone --) Amides, such as a methyl ethyl ketone (dimethylformamide, dimethylacetamide, etc.), Carbonate (ethylene carbonate, propylene carbonate, etc.), ester (ethyl acetate, diethyl maleate, etc.) and lactone (gamma-butyrolactone --) Sulfur content solvents (dimethyl sulfoxide, sulfolane, etc.), halogenated hydrocarbon (chloroform, dichloromethane, etc.), and hydrocarbons (a hexane, toluene, etc.) are mentioned, and delta-valerolactones etc. are water, monoalcohol, and the mono-ether preferably. Two or more sorts of these solvents may be used.
[0012] The above-mentioned mixed solution contains an oxidizer (a-2) 0.001 to 5 mol/l still more preferably 0.0001 to 10 mol/l preferably 0.05 to 5 mol/l still more preferably, including a monomer (a-1) 0.01 to 10 mol/l. That is, based on the above-mentioned mixed solution, the above-mentioned mixed solution contains 0.05 or more mol/l (a-1) of monomers still more preferably, and contains them 5 or less mol/l still more preferably 10 or less mol/l preferably 0.01 or more mol/l. Moreover, based on the above-mentioned mixed solution, the above-mentioned mixed solution contains still more preferably 0.0001 mols /or more of 0.001 or more mol/l of oxidizers (a-2)l., and contains them 5 or less mol/l still more preferably 10 or less mol/l preferably. Viscosity (temperature of 25 degrees C) is 0.1 - 10,000 mPa-s preferably, and is 0.1 - 500 mPa-s still more preferably. That is, viscosity (temperature of 25 degrees C) is 0.1 or more mPa-s preferably, is 10,000 or less mPa-s preferably, and is 500 or less mPa-s still more preferably. well-known polymerization conditions are sufficient as polymerization conditions, it is a -100 degrees C - 200 degrees C temperature requirement preferably, and a polymerization is performed for 1 minute - 48 hours -- especially, it is the range of 0 degree C - 150 degrees C preferably, and carries out for 1 - 60 minutes. As for this polymerization, it may be desirable to carry out on a capacitor element in the above-mentioned combination, and a polymerization may be repeated two or more times.

[0013] (II) In the case of the approach this polymerization by the gaseous-phase chemistry polymerization, the oxidation polymerization performed by (I) is performed in a gaseous phase, and it installed and postpolymerizes the capacitor element immersed in the solution preferably included beforehand (a-2) in the gaseous phase containing (a-1).
[0014] (a-1), (a-2), a solvent, etc. can use the same thing as what was mentioned by (I), and the desirable thing of them is the same as that of (I). The above-mentioned oxidizer solution contains (a-2) 0.001 to 5 mol/l still more preferably 0.0001 to 10 mol/l preferably. That is, 0.001 or more mol/l of 0.0001 or more mol/l of 10 or less mol/l of the five mols /or less of the above-mentioned oxidizer solutions is includedl. still more preferably preferably still more preferably, including (a-2) preferably. well-known polymerization conditions are sufficient as polymerization conditions, it is a -60 degrees C - 200 degrees C temperature requirement preferably, and a polymerization is performed for 1 minute - 48 hours -- it carries out for 1 - 60 minutes in -15 degrees C - 25 degrees C still more preferably. As for this polymerization, it may be desirable to carry out on a capacitor element in the above-mentioned combination, and a polymerization may be repeated two or more times.
[0015] (III) the case of the approach this polymerization by electrolytic polymerization -- (a-1) -- being desirable (a-2) -- the polymerization of the capacitor element is energized [it is immersed and] and carried out to the solution to contain. (I) And (III) is electrolytic polymerization although the polymerization of (II) is a chemistry oxidation polymerization.
[0016] (a-1), (a-2), and a solvent can use the same thing as the above-mentioned (I) and (II), and the desirable thing of (a-1) is the same as (I). The desirable things of (a-2) are proton acid and its salt, a peroxy acid, and its salt, and especially desirable things are the aromatic series sulfonic-acid sodium of carbon numbers 7-30, the aromatic series sulfonic-acid ammonium of carbon numbers 7-30, and an ammonium perchlorate.
[0017] The above-mentioned solution contains an oxidizer (a-2) for a monomer (a-1) 0.0001 to 5 mol/l still more preferably 0.00001 to 10 mol/l preferably 0.01 to 10 mol/l including 0.05 - 5 mol/l still more preferably. That is, based on the above-mentioned solution, the above-mentioned solution contains 0.05 or more mol/l (a-1) of monomers still more preferably, and contains them 5 or less mol/l still more preferably 10 or less mol/l preferably 0.01 or more mol/l. Moreover, based on the above-mentioned solution, the above-mentioned solution contains 0.0001 or more mol/l (a-2) of oxidizers still more preferably, and contains them 5 or less mol/l still more preferably 10 or less mol/l preferably 0.00001 or more mol/l.
[0018] well-known polymerization conditions are sufficient as polymerization conditions, and they are energized preferably in a -100 degrees C - 200 degrees C temperature requirement, and a polymerization is performed for 1 minute - 48 hours -- it carries out for [1 minute -] 60 minutes in 10 degrees C - 100 degrees C still more preferably.
[0019] As for a polymerization, it is desirable to carry out by electrolyzing with a potentiostatic process or a galvanostatic process on a capacitor element in the above-mentioned combination, and polymerization **** is formed on a capacitor element. In a potentiostatic process, it is the potential range of 0.1 - 5Vvs.S C E (saturation calomel electrode) preferably, and a polymerization is preferably performed with a galvanostatic process at the current density of 0.01 - 100 mA/cm2. In addition, a polymerization may be repeated two or more times.
[0020] (I) Except for carrying out a polymerization independently and introducing into a capacitor element, although the polymerization object (A-1) obtained by -(III) is already on a capacitor element since it performed the polymerization on the capacitor element.
[0021] The polymerization object formed with these polymerization methods is a conjugated-double-bond polymer (A-1), and may dope and use a dopant (A-2) for this polymer further. Between (A-1) and (A-2), charge transfer happens and a dope (or it is called doping) raises the conductivity of (A-1). A dopant is the electronic receptiveness or the electron-donative reagent which gives conductivity to (A-1). When electronic receptiveness or an electron-donative component is contained in the oxidizer (a-2), it acts also as a dopant at the time of a polymerization, and the polymerization object formed with the above-mentioned polymerization method in this case is doped by a polymerization and coincidence. For

example, when a transition-metals salt is used as an oxidizer, transition metals receive an electron from a polymer, the oxidation number decreases, and a counter ion gives conductivity to a polymer in electronic supply.

[0022] The following are mentioned as (A-2).

(1) proton acid; -- inorganic proton acid (a hydrochloric acid, a sulfuric acid, a nitric acid, and fluosulfonic acid --) with a; molecular weight of less than 1,000 low-molecular organic-acids [, such as chlorosulfuric acid, a phosphoric acid, a hydrofluoric acid, and the Lynn hydrofluoric acid,] [phenols (a phenol --) The aliphatic carboxylic acid of the carbon numbers 1-30, such as a naphthol, (an acetic acid, proton acid, etc.), the aromatic carboxylic acid (a benzoic acid, phthalic acid, etc.) of carbon numbers 7-30, and the aliphatic series sulfonic acid (methansulfonic acid --) of carbon numbers 1-30], such as aromatic series sulfonic acids (benzenesulfonic acid, p-toluenesulfonic acid, etc.) of carbon numbers 7-30, such as a propane sulfonic acid; giant-molecule organic acids of weight average molecular weight 1,000-1,000,000 (polystyrene sulfonate, polyvinyl sulfonic acid, etc.) etc.;

[0023] (2) A halogen and a halogenide; a bromine, iodine, an iodation bromine, arsenic pentafluoride, 5 antimony fluoride, silicon tetrafluoride, a phosphorus pentachloride, phosphorus pentafluoride, an aluminum chloride, the aluminium bromide, ferric chloride, a copper chloride, etc. Proton acid is [among these] desirable, still more desirable things are a hydrochloric acid, a sulfuric acid, the aliphatic carboxylic acid of carbon numbers 1-30, the aromatic carboxylic acid of carbon numbers 7-30, the aliphatic series sulfonic acid of carbon numbers 1-30, and the aromatic series sulfonic acid of carbon numbers 7-30, and especially desirable things are the aliphatic carboxylic acid of carbon numbers 1-30, the aromatic carboxylic acid of carbon numbers 7-30, the aliphatic series sulfonic acid of carbon numbers 1-30, and the aromatic series sulfonic acid of carbon numbers 7-30. In addition, the dopant (A-2) in this invention may use a kind or two sorts or more.

[0024] Once forming addition of (A-2) (A-1), although you may carry out by the approach chemically or electrochemically, it is good well-known to use an oxidizer together as mentioned above preferably in the case of a polymerization, and to dope to a polymerization and coincidence. By the chemical approach, it dopes by making (A-2) mix or react with (A-1) with a gaseous phase or a solution, and in an electrochemical process, (A-1) is immersed in the solution which dissolved (A-2), potential is applied by using (A-1) as an electrode, and it dopes electrochemically. It is (A) preferably formed on the capacitor element. Thus, a conductive polymer (A) is formed, and the conductivity is 10-5 - 105 S/cm preferably, and is 10-2 - 105 S/cm still more preferably. That is, the conductivity is 10 to 2 or more S/cm still more preferably, and is 105 or less S/cm preferably 10 to 5 or more S/cm.

[0025] In this invention, organic-acid onium salt (B) is formed from an onium cation and an organic-acid anion. It is desirable that it is the organic-acid salt of an onium cation as (B), and is organic-acid onium salt which is one sort chosen from the group of the cation which an onium cation specifically turns into from the 4th class ammonium, 3rd class sulfonium, the 4th class phosphonium, and the 3rd class oxonium, or two sorts or more, and is one or more sorts chosen from the group of the anion excluding the proton from the organic acid which an organic-acid anion becomes from a carboxylic acid, a sulfonic acid, phenols, monochrome or dialkyl phosphoric ester, a boron complex.

[0026] The example of the onium cation used for ** (B) is indicated below.

(I) As the 4th class ammonium cation, following - (I-1) (I-10) is mentioned.

The 4th class ammonium of an aliphatic series system which has carbon numbers 4-30 or the alkyl beyond it, and/or an alkenyl radical; Tetramethylammonium, (I-1) Ethyl trimethylammonium, diethyl dimethylannmonium, triethyl methylammonium, Trimethyl ethylammonium, tetraethylammonium, trimethyl propyl ammonium, Dimethyl dipropyl ammonium, ethyl methyl dipropyl ammonium, butyl trimethylammonium, dimethyl dibutyl ammonium, tetrabutylammonium, tetra-hexyl ammonium, trimethyl DESHIRU ammonium, etc.;

[0027] Carbon numbers 6-30 or the 4th class ammonium of an aromatic series system beyond it; (I-2) Trimethyl phenyl ammonium, dimethylethyl phenyl ammonium, triethyl phenyl ammonium, etc.;

[0028] Carbon numbers 3-30 or the 4th class ammonium of alicyclic beyond it; (I-3) N and N-dimethyl PIROJINIUMU, N-ethyl-N-methyl pyrrolidinium, N, and N-diethyl pyrrolidinium, N, and N-dimethyl

mol HORINIUMU, N-ethyl-N-methyl mol HORINIUMU, N, and N-diethyl mol HORINIUMU, N, and N-dimethyl piperidinium, N, and N-diethyl piperidinium etc.;
[0029] Carbon numbers 3-30 or imidazolinium beyond it; 1, 2, 3-trimethyl imidazolinium, (I-4) 1, 2, 3, 4-tetramethyl imidazolinium, 1 and 3, 4-trimethyl-2-ethyl imidazolinium, 1, the 3-dimethyl -2, 4-diethyl imidazolinium, 1, the 2-dimethyl -3, 4-diethyl imidazolinium, 1, 2-dimethyl-3-ethyl imidazolinium, 1, 2 and 3, 4-tetraethyl imidazolinium, 1, 2, 3-triethyl imidazolinium, 4-cyano - 1, 2, 3-trimethyl imidazolinium, 2-cyano methyl -1, 3-dimethyl imidazolinium, 4-acetyl - 1, 2, 3-trimethyl imidazolinium, 3-acetyl methyl -1, 2-dimethyl imidazolinium, 4-methyl cull baud oxymethyl - 1, 2, 3-trimethyl imidazolinium, 3-methoxymethyl -1, 2-dimethyl imidazolinium, 4-formyl - 1, 2, 3-trimethyl imidazolinium, 3-formyl methyl -1, 2-dimethyl imidazolinium, 3-hydroxyethyl -1, 2-dimethyl imidazolinium, 4-hydroxymethyl - 1, 2, 3-trimethyl imidazolinium, etc.;
[0030] Carbon numbers 3-30 or imidazolium beyond it; 1, 3-dimethyl imidazolium, (I-5) 1-ethyl-3-methyl imidazolium, 1-methyl-3-ethyl imidazolium, 1, 2, 3-trimethyl imidazolium, 1, 3-dimethyl-2-ethyl imidazolium, 1, 2-dimethyl-3-ethyl-imidazolium, 1 and 2, 3-triethyl imidazolium, 1, 2, 3, 4-tetraethyl imidazolium, 1, 3-dimethyl-2-phenyl imidazolium, 1, 3-dimethyl-2-benzyl imidazolium, the 1-benzyl -2, 3-dimethyl-imidazolium, 4-cyano - 1, 2, 3-trimethyl imidazolium, 3-cyano methyl -1, 2-dimethyl imidazolium, 4-acetyl - 1, 2, 3-trimethyl imidazolium, 3-acetyl methyl -1, 2-dimethyl imidazolium, 4-methyl cull baud oxymethyl - 1, 2, 3-trimethyl imidazolium, 3-methyl cull baud oxymethyl -1, 2-dimethyl imidazolium, 4-methoxy - 1, 2, 3-trimethyl imidazolium, 4-formyl - 1, 2, 3-trimethyl imidazolium, 3-formyl methyl -1, 2-dimethyl imidazolium, 3-hydroxyethyl -1, 2-dimethyl imidazolium, 2-hydroxyethyl -1, 3-dimethyl imidazolium, N, and N'-dimethylbenzo imidazolinium, N, and N'- diethyl benzoimidazolinium and N-methyl-N'-ethylbenzo imidazolinium etc.;
[0031] Carbon numbers 4-30 or tetrahydro pilus midge NIUMU beyond it; 1, 3-dimethyl tetrahydro pilus MIJINIUMU, (I-6) 1, 2, 3-trimethyl tetrahydro pilus MIJINIUMU, 1, 2 and 3, 4-tetramethyl tetrahydro pilus MIJINIUMU, The 8-methyl -1, 8-diazabicyclo [5, 4, 0]-7-UNDESENIUMU, The 5-methyl -1, 5-diazabicyclo [4, 3, 0]-5-NONENIUMU, 4-cyano - 1, 2, 3-trimethyl tetrahydro pilus MIJINIUMU, 3-cyano methyl -1, 2-dimethyl tetrahydro pilus MIJINIUMU, 4-acetyl - 1, 2, 3-trimethyl tetrahydro pilus MIJINIUMU, 3-acetyl methyl -1, 2-dimethyl tetrahydro pilus MIJINIUMU, 4-methyl cull baud oxymethyl - 1, 2, 3-trimethyl tetrahydro pilus MIJINIUMU, 4-methoxy - 1, 2, 3-trimethyl tetrahydro pilus MIJINIUMU, 3-methoxymethyl -1, 2-dimethyl tetrahydro pilus MIJINIUMU, 4-hydroxymethyl - 1, 2, 3-trimethyl tetrahydro pilus MIJINIUMU, 2-hydroxyethyl -1, 3-dimethyl tetrahydro pilus MIJINIUMU, etc.;
[0032] (I-7) dihydropilus midge NIUMU; beyond carbon numbers 4-30 or it -- 1, the 3-dimethyl -2, 4- or -2, 6-dihydropilus midge NIUMU, and [-- it writes 1, the 3-dimethyl -2, and 4(6)-dihydropilus midge NIUMU [these], and the same expression as the following is used.] 1, 2, 3-trimethyl -2, 4(6)-dihydropilus midge NIUMU, 1, 2, 3, 4-tetramethyl - 2, 4(6)-dihydropilus midge NIUMU, 1, 2, 3, 5-tetramethyl - 2, 4(6)-dihydropilus midge NIUMU, The 8-methyl -1, 8-diazabicyclo [5, 4, 0]-7, 9(10)-undeca JIENIUMU, The 5-methyl -1, 5-diazabicyclo [4, 3, 0]-5, 7(8)-nona JIENIUMU, 2-cyano methyl -1, the 3-dimethyl -2, 4(6)-dihydropilus midge NIUMU, 3-acetyl methyl -1, the 2-dimethyl -2, 4(6)-dihydropilus midge NIUMU, 4-methyl cull baud oxymethyl - 1, 2, 3-trimethyl -2, 4(6)-dihydropilus midge NIUMU, 4-methoxy - 1, 2, 3-trimethyl -2, 4(6)-dihydropilus midge NIUMU, 4-formyl - 1, 2, 3-trimethyl -2, 4(6)-dihydropilus midge NIUMU, 3-hydroxyethyl -1, the 2-dimethyl -2, 4(6)-dihydropilus midge NIUMU, 2-hydroxyethyl -1, the 3-dimethyl -2, 4(6)-hydronalium pilus midge NIUMU, etc.;
[0033] Guanidinium which has carbon numbers 3-30 or an imidazolinium frame beyond it; (I-8) 2-dimethylamino - 1, 3, 4-trimethyl imidazolinium, 2-diethylamino - 1, 3, 4-trimethyl imidazolinium, 2-diethylamino -1, 3-dimethyl-4-ethyl imidazolinium, The 2-dimethylamino-1-methyl -3, 4-diethyl imidazolinium, 2-diethylamino - 1, 3, 4-tetraethyl imidazolinium, 2-dimethylamino -1, 3-dimethyl imidazolinium, 2-diethylamino -1, 3-dimethyl imidazolinium, 2-diethylamino -1, 3-diethyl imidazolinium, 1, 5 and 6, 7-tetrahydro -1 and 2-dimethyl-2H-imide [1, 2a] imidazolinium, 1, 5, 6, 7-tetrahydro -1 and 2-dimethyl-2H-pyrimide [1, 2a] imidazolinium, 1, 5-dihydro-1 and 2-dimethyl-2H-pyrimide [1, 2a] imidazolinium, 2-dimethylamino-3-cyano methyl-1-methyl imidazolinium, The 2-

dimethylamino-4-acetyl -1, 3-dimethyl imidazolinium, 2-dimethylamino-4-methyl cull baud oxymethyl -1, 3-dimethyl imidazolinium, 2-dimethylamino-3-methyl cull baud oxymethyl-1-methyl imidazolinium, 2-dimethylamino-3-methoxymethyl-1-methyl imidazolinium, The 2-dimethylamino-4-formyl -1, 3-dimethyl imidazolinium, 2-dimethylamino-3-hydroxyethyl-1-methyl imidazolinium, 2-dimethylamino-4-hydroxymethyl -1, 3-dimethyl imidazolinium, etc.;

[0034] Guanidinium which has carbon numbers 3-30 or an imidazolium frame beyond it; (I-9) 2-dimethylamino - 1, 3, 4-trimethyl imidazolium, 2-diethylamino - 1, 3, 4-trimethyl imidazolium, 2-diethylamino -1, 3-dimethyl-4-ethyl imidazolium, The 2-diethylamino-1-methyl -3, 4-diethyl imidazolium, 2-diethylamino - 1, 3, 4-tetraethyl imidazolium, 2-dimethylamino -1, 3-dimethyl imidazolium, 2-dimethylamino-1-ethyl-3-methyl imidazolium, 2-diethylamino -1, 3-diethyl imidazolium, 1, 5, 6, 7-tetrahydro -1 and 2-dimethyl-2H-imide [1, 2a] imidazolium, 1, 5, 6, 7-tetrahydro -1 and 2-dimethyl-2H-pyrimide [1, 2a] imidazolium, 1, 5-dihydro-1 and 2-dimethyl-2H-pyrimide [1, 2a] imidazolium, 2-dimethylamino-3-cyano methyl-1-methyl imidazolium, The 2-dimethylamino-4-acetyl -1, 3-dimethyl imidazolinium, 2-dimethylamino-4-methyl cull baud oxymethyl -1, 3-dimethyl imidazolium, The 2-dimethylamino-4-methoxy -1, 3-dimethyl imidazolium, 2-dimethylamino-3-methoxymethyl-1-methyl imidazolium, 2-dimethylamino-3-formyl methyl-1-methyl imidazolium, 2-dimethylamino-4-hydroxymethyl -1, 3-dimethyl imidazolium, etc.;

[0035] Guanidinium which has carbon numbers 4-30 or a tetrahydro pilus midge NIUMU frame beyond it; (I-10) 2-dimethylamino - 1, 3, 4-trimethyl tetrahydro pilus MIJINIUMU, 2-diethylamino - 1, 3, 4-trimethyl tetrahydro pilus MIJINIUMU, 2-diethylamino -1, 3-dimethyl-4-ethyl tetrahydro pilus MIJINIUMU, The 2-diethylamino-1-methyl -3, 4-diethyl tetrahydro pilus MIJINIUMU, 2-dimethylamino -1, 3-dimethyl tetrahydro pilus MIJINIUMU, 2-diethylamino -1, 3-dimethyl tetrahydro pilus MIJINIUMU, 2-diethylamino -1, 3-diethyl tetrahydro pilus MIJINIUMU, 1, 3, 4, 6, 7, 8-hexahydro -1, 2-dimethyl-2H-imide [1,a [2]] pilus midge NIUMU, 1, 3, 4, 6, 7, 8-hexahydro -1, 2-dimethyl-2H-pyrimide [1,a [2]] pilus midge NIUMU, 2, 3, 4, 6-tetrahydro - 1, 2-dimethyl-2H-pyrimide [1,a [2]] pilus midge NIUMU, 2-dimethylamino-3-cyano methyl-1-methyl tetrahydro pilus MIJINIUMU, The 2-dimethylamino-4-acetyl -1, 3-dimethyl tetrahydro pilus MIJINIUMU, 2-dimethylamino-4-methyl cull baud oxymethyl -1, 3-dimethyl tetrahydro pilus MIJINIUMU, 2-dimethylamino-3-methyl cull baud oxymethyl-1-methyl tetrahydro pilus MIJINIUMU, 2 - Dimethylamino-3-methoxymethyl-1-methyl tetrahydro pilus MIJINIUMU, The 2-dimethylamino-4-formyl -1, 3-dimethyl tetrahydro pilus MIJINIUMU, 2 - Dimethylamino-3-hydroxyethyl-1-methyl tetrahydro pilus MIJINIUMU, 2-dimethylamino-4-hydroxymethyl -1, 3-dimethyl tetrahydro pilus MIJINIUMU, etc.;

[0036] Guanidinium which has carbon numbers 4-30 or a dihydropilus midge NIUMU frame beyond it; (I-11) 2-dimethylamino - 1, 3, 4-trimethyl -2, 4(6)-dihydropilus midge NIUMU, 2-diethylamino - 1, 3, 4-trimethyl -2, 4(6)-dihydropilus midge NIUMU, The 2-dimethylamino-1-methyl -3, the 4-diethyl -2, 4(6)-dihydropilus midge NIUMU, The 2-diethylamino-1-methyl -3, the 4-diethyl -2, 4(6)-dihydropilus midge NIUMU, 2-diethylamino - 1, 3, 4-tetraethyl -2, 4(6)-dihydropilus midge NIUMU, 2-diethylamino -1, the 3-dimethyl -2, 4(6)-dihydropilus midge NIUMU, The 2-dimethylamino-1-ethyl-3-methyl -2, 4(6)-dihydropilus midge NIUMU, 1, 6, 7, 8-tetrahydro - 1, 2-dimethyl-2H-imide [1,a [2]] pilus midge NIUMU, 1, 6-dihydro - 1, 2-dimethyl-2H-imide [1,a [2]] pilus midge NIUMU, 1, 6-dihydro - 1, 2-dimethyl-2H-pyrimide [1,a [2]] pilus midge NIUMU, 2-dimethylamino-4-cyano - 1, the 3-dimethyl -2, 4(6)-dihydropilus midge NIUMU, The 2-dimethylamino-4-acetyl -1, the 3-dimethyl -2, 4(6)-dihydropilus midge NIUMU, The 2-dimethylamino-3-acetyl methyl-1-methyl -2, 4(6)-dihydropilus midge NIUMU, 2 - The dimethylamino-3-methyl cull baud oxymethyl-1-methyl -2, 4(6)-dihydropilus midge NIUMU, The 2-dimethylamino-4-methoxy -1, the 3-dimethyl -2, 4(6)-dihydropilus midge NIUMU, The 2-dimethylamino-4-formyl -1, 3-dimethyl tetrahydro pilus MIJINIUMU, 2-dimethylamino-3-formyl methyl-1-methyl tetrahydro pilus MIJINIUMU, 2-dimethylamino-4-hydroxymethyl -1, the 3-dimethyl -2, 4(6)-dihydropilus midge NIUMU, etc.

[0037] (II) Following - (II-1) (II-3) is mentioned as the 3rd class sulfonium cation.

The 3rd class sulfonium of an aliphatic series system which has carbon numbers 1-30, or the alkyl

and/or the alkenyl radical beyond it; (II-1) Trimethyl sulfonium, triethyl sulfonium, ethyl dimethyl sulfonium, diethyl methyl sulfonium, etc.;
Carbon numbers 6-30 or the 3rd class sulfonium of an aromatic series system beyond it; (II-2) Phenyl dimethyl sulfonium, phenylethyl methyl sulfonium, phenylmethyl benzyl sulfonium, etc.;
Carbon numbers 3-30 or the 3rd class sulfonium of alicyclic beyond it; (II-3) Methylthio RANIUMU, phenylthio RANIUMU, methyl thia NIUMU, etc.;
[0038] (III) Following - (III-1) (III-3) is mentioned as the 4th class phosphonium cation.
The 4th class phosphonium of an aliphatic series system which has carbon numbers 1-30 or an alkyl group beyond it, and/or an alkenyl radical; Tetramethylphosphonium, (III-1) Tetraethyl phosphonium, tetra-propyl phosphonium, tetrabuthyl phosphonium, Methyl triethyl phosphonium, methyl TORIPURO pill phosphonium, Methyl tributyl phosphonium, dimethyl diethyl phosphonium, trimethyl ethyl phosphonium, Trimethyl propyl phosphonium, ethyl TORIPURO pill phosphonium, Ethyl tributyl phosphonium, diethyl dibutyl phosphonium, triethyl butyl phosphonium, propyl tributyl phosphonium, dipropyl dibutyl phosphonium, TORIPURO pill butyl phosphonium, etc.;
Carbon numbers 6-30 or the 4th class phosphonium of an aromatic series system beyond it; (III-2) Triphenylmethyl phosphonium, diphenyl dimethyl phosphonium, triphenyl benzyl phosphonium, etc.;
Carbon numbers 3-30 or the 4th class phosphonium of alicyclic beyond it; (III-3) 1 and 1-dimethyl phospho RANIUMU, 1-methyl-1-ethyl phospho RANIUMU, 1, and 1-diethyl phospho RANIUMU, 1, and 1-dimethyl phospho RINANIUMU, 1-methyl-1-ethyl phospho RINANIUMU, 1, and 1-diethyl phospho RINANIUMU, 1, and 1-pentamethylene phospho RINANIUMU etc.;
[0039] (IV) Following - (IV-1) (IV-3) is mentioned as the 3rd class oxonium cation.
The 3rd class oxonium of an aliphatic series system which has carbon numbers 1-30 or the alkyl beyond it, and/or an alkenyl radical; (IV-1) Trimethyl oxonium, triethyl oxonium, ethyl dimethyl oxonium, diethyl methyl oxonium, etc.;
Carbon numbers 6-30 or the 3rd class oxonium of an aromatic series system beyond it; (IV-2) Phenyl dimethyl oxonium, phenylethyl methyl oxonium, phenylmethyl benzyl oxonium, etc.;
Carbon numbers 3-30 or the 3rd class oxonium of alicyclic beyond it; (IV-3) Methyl oxo-RANIUMU, phenyl oxo-RANIUMU, methyl OKISANIUMU, etc.;
[0040] The 4th class ammonium cation is [among these] desirable. Still more desirable one Carbon numbers 4-30 or the aliphatic series system ammonium beyond it, carbon numbers 3-30, or the imidazolinium beyond it, They are carbon numbers 3-30 or imidazolium beyond it. Especially a desirable thing Trimethyl ethylammonium, dimethyl diethyl ammonium, triethyl methylammonium, They are 1, 2, 3, 4-tetramethyl imidazolinium, 1, 2-dimethyl-3-ethyl imidazolinium, 1-ethyl-3-methyl imidazolium, and 1-methyl-3-ethyl imidazolium. These onium cations may use a kind or two sorts or more.
[0041] The example of the organic acid which forms the pair anion of ** (B) is indicated below.
(I) As a carboxylic acid, following - (I-1) (I-4) is mentioned.
(I-1) Saturation and partial saturation aliphatic carboxylic acid beyond carbon numbers 1-30 or it; Univalent aliphatic carboxylic acid; (I-1-1) Unsaturated carboxylic acid, such as saturation carboxylic acids, such as a formic acid, an acetic acid, a propionic acid, butanoic acid, an isobutyric acid, a valeric acid, a caproic acid, enanthic acid, a caprylic acid, a BERARUGON acid, a lauryl acid, a myristic acid, stearic acid, and behenic acid, an acrylic acid, a methacrylic acid, and oleic acid etc.;
Aliphatic carboxylic acid more than divalent; Oxalic acid, a malonic acid, (I-1-2) A succinic acid, a glutaric acid, an adipic acid, an azelaic acid, sebacic acid, 1, 10-Deccan dicarboxylic acid, Straight chain saturation dicarboxylic acid, such as 1, 12-Deccan dicarboxylic acid, a PURASHIRU acid, 1, and 15-PENTA dicarboxylic acid, A methylmalonic acid, an ethyl malonic acid, a butyl malonic acid, 3-methyl adipic acid, 1, 6-Deccan dicarboxylic acid, diethyl malonic-acid, 2, and 2- or 2, 3-dimethyl succinic acid, 2-ethyl-3-methyl succinic-acid, 2, and 2- or 2, and 3- or 2, and 4- or 3, and 3-dimethyl glutaric acid, Branching saturation carboxylic acids, such as 3-ethyl-3-methyl glutaric-acid, 2-butyl octanedioic acid, 5, and 6-Deccan dicarboxylic acid, Partial saturation dicarboxylic acid, such as tricarballylic acid, 1 and 6, 11- or 1 and 10, 11- or 5 and 6, 11-pentadecane tricarboxylic acid, 1, 2 and 3, 4-butane

tetracarboxylic acid, a maleic acid, boletic acid, and a citraconic acid etc.;
Oxy-aliphatic carboxylic acid; (I-1-3) A glycolic acid, a lactic acid, tartaric acid, etc.;
Thio aliphatic carboxylic acid; (I-1-4) Thiodipropionic acid etc.;
[0042] (I-2) Carbon numbers 7-30 or aromatic carboxylic acid beyond it;
Univalent aromatic carboxylic acid; (I-2-1) A benzoic acid, a cinnamic acid, naphthoic acid, etc.;
Aromatic carboxylic acid more than divalent; (I-2-2) A phthalic acid, isophthalic acid, a terephthalic acid, trimellitic acid, pyromellitic acid, etc.;
Oxy-aromatic carboxylic acid; (I-2-3) A salicylic acid, mandelic acid, etc.;
[0043] Carbon numbers 3-30 or the alicyclic carboxylic acid beyond it; Cyclobutene -1, 2-dicarboxylic acid, (I-3) Cyclopentene -1, 2-dicarboxylic acid, 1, and 2- or 1, 4-cyclohexane dicarboxylic acid, Hepta-[bicyclo [2, 2, 1] / 2- or the 3-methyl -1 4-cyclohexane dicarboxylic acid, a furan -2, 3-dicarboxylic acid the bicyclo [2 2, 1] hepta--2-en -2, 3-dicarboxylic acid,] - 2, the 5-diene -2, 3-dicarboxylic acid, etc.;
[0044] The polymer and copolymer of the monomer which has a carboxyl group; (I-4) The carboxylic acid of the carbon numbers 3-30 which have a carboxyl group and polymerization nature double bonds, such as an acrylic acid (meta), a cinnamic acid, and a vinyl benzoic acid, as a polymerization nature monomer which has a carboxyl group is mentioned. By the approach that polymerization conditions etc. are well-known, it is good and polymerization degree is 20-1,000 preferably [it is desirable and] to 16-10,000, and a pan. Things desirable as a carboxylic acid among the above are an adipic acid, 1, 6-Deccan dicarboxylic acid, a phthalic acid, and a benzoic acid.
[0045] (II) Following - (II-1) (II-3) is mentioned as a sulfonic acid.
(II-1) The saturation and the partial saturation aliphatic series sulfonic acid beyond carbon numbers 1-30 or it;
A univalent aliphatic series sulfonic acid; Methansulfonic acid, ethane sulfonic acid, (II-1-1) A propane sulfonic acid, an isopropyl sulfonic acid, a butane sulfonic acid, An isobutyl sulfonic acid, t-butyl sulfonic acid, a pentane sulfonic acid, An isopentyl sulfonic acid, a hexane sulfonic acid, a nonane sulfonic acid, The Deccan sulfonic acid, an undecane sulfonic acid, a dodecane sulfonic acid, a tridecane sulfonic acid, Partial saturation sulfonic acids, such as saturation carboxylic acids, such as a tetradecane sulfonic acid, n-octyl sulfonic acid, a dodecyl sulfonic acid, and a cetyl sulfonic acid, an ethylene sulfonic acid, a 1-propene-1-sulfonic acid, a benzyl sulfonic acid, and phenyl ethane sulfonic acid etc.;
The aliphatic series sulfonic acid more than divalent; (II-1-2) Methionic acid, 1, and 1-ethane-disulfonic-acid, 1, 2-ethane-disulfonic-acid, 1, and 1-propane disulfon acid, 1, 3-propane disulfon acid, polyvinyl sulfonic acid, etc.;
Oxy-aliphatic series sulfonic acid; (II-1-3) Isethionic acid, 3-oxy--propane sulfonic acid, etc.;
Sulfo aliphatic carboxylic acid; (II-1-4) A sulfo acetic acid, sulfo succinic acid, etc.;
[0046] (II-2) Carbon numbers 6-30 or aromatic series sulfonic acid beyond it;
A univalent monocycle type aromatic series sulfonic acid; (II-2-1) Benzenesulfonic acid, p-toluenesulfonic acid, o-toluenesulfonic acid, m-toluenesulfonic acid, an O-xylene-4-sulfonic acid, a meta xylene-4-sulfonic acid, 4-dodecylbenzenesulfonic acid, 4-octyl benzenesulfonic acid, 2-methyl-5-isopropyl benzenesulfonic acid, etc.;
A univalent polycyclic-aromatics sulfonic acid; (II-2-2) Alkyl naphthalene sulfonic acids, such as a naphthalene sulfonic acid and a triisopropyl naphthalene sulfonic acid, an anthracene sulfonic acid, phenanthrene sulfonic acid, etc.;
The aromatic series sulfonic acid more than divalent; (II-2-3) m-benzene disulfon acid, 1, 4-naphthalene sulfonic acid, 1, 5-naphthalene disulfon acid, 1, 6-naphthalene disulfon acid, 2, 6-NAFETA range sulfonic acid, 2, 7-naphthalene disulfon acid, sulfonated polystyrene, etc.;
Oxy-aromatic series sulfonic acid; A phenol-2-sulfonic acid, (II-2-4) A phenol-3-sulfonic acid, a phenol-4-sulfonic acid, an anisole-o-sulfonic acid, An anisole-m-sulfonic acid, a phenetole-o-sulfonic acid, a phenetole-m-sulfonic acid, A phenol -2, 4-disulfon acid, phenol - 2, 4, 6-Tori sulfonic acid, An anisole - 2, 4-disulfon acid, a phenetole -2, 5-disulfon acid, A 2-oxy-toluene-4-sulfonic acid, a pyrocatechin-4-sulfonic acid, A Bela Thor-4-sulfonic acid, a resorcinol-4-sulfonic acid, a 2-oxy--1-methoxybenzene-4-sulfonic acid, 1, 2-dioxy benzene -3, 5-disulfon acid, resorcinol -4, 6-disulfonic acid, a hydroquinone

sulfonic acid, a hydroquinone -2, 5-disulfon acid, 1 and 2, 3-TORIOKISHI benzene-4-sulfonic acid, etc.;
Sulfo aromatic carboxylic acid; o-sulfobenzonic acid, m-sulfobenzonic acid, (II-2-5) p-sulfobenzonic acid, 2, a 4-disulfo benzoic acid, 3-sulfo phthalic acid, 3, a 5-disulfo phthalic acid, 4-sulfoisophtharate, 2-sulfo terephthalic acid, 2-methyl-4-sulfobenzonic acid, the 2-methyl -3, a 5-disulfo benzoic acid, 4-propyl-3-sulfobenzonic acid, 2 and 4, 6-trimethyl-3-sulfobenzonic acid, a 2-methyl-5-sulfo terephthalic acid, 5-sulfosalicylic acid, 3-oxy--4-sulfobenzonic acid, etc.;
Thio aromatic series sulfonic acid; (II-2-6) A thiophenol sulfonic acid, a thioanisole-4-sulfonic acid, thio phenetole-4-sulfonic acid, etc.;
The aromatic series sulfonic acid which has a functional group in addition to this; A benzaldehyde-o-sulfonic acid, (II-2-7) A benzaldehyde -2, 4-disulfon acid, an acetophenone-o-sulfonic acid, An acetophenone -2, 4-disulfon acid, a benzophenone-o-sulfonic acid, A benzophenone -3, a 3'-disulfon acid, a 4-aminophenol-3-sulfonic acid, An anthraquinone-1-sulfonic acid, anthraquinone -1, 5-disulfon acid Anthraquinone -1, 8-disulfon acid, anthraquinone -2, 6-disulfonic acid, 2-methyl anthraquinone-1-sulfonic acid, etc.;
[0047] Carbon numbers 3-30 or the alicyclic carboxylic acid beyond it; (II-3) Things desirable as the sulfonic acids among; above, such as a cyclopentane sulfonic acid and a cyclohexane sulfonic acid, are p-toluenesulfonic acid, a triisopropyl naphthalene sulfonic acid, a naphthalene sulfonic acid, and a phenol-4-sulfonic acid.
[0048] (III) Following (III-1) is mentioned as phenols.
(III-1) The permutation or unsubstituted phenol beyond carbon numbers 6-30 or it;
A univalent phenol; (III-1-1) A phenol, a naphthol, a cyclohexyl phenol, cresol, a xylenol, ethylphenol, n and an isopropyl phenol, n and an isoamyl phenol, iso nonyl phenol, an iso dodecyl phenol, an eugenol, guaiacol, etc.;
The phenol more than divalent; (III-1-2) A catechol, resorcinol, pyrogallol, phloroglucine, etc.;
[0049] (IV) Following - (IV-1) (IV-2) is mentioned as monochrome or dialkyl phosphoric ester.
Carbon numbers 1-30 or monoalkyl phosphate ester beyond it; (IV-1) Methylphosphoric acid ester, isopropyl phosphoric ester, butyl phosphoric ester, 2-ethylhexyl phosphoric ester, isodecyl phosphoric ester, etc.;
Carbon numbers 2-30 or dialkyl phosphoric ester beyond it; (IV-2) Dimethyl phosphoric ester, diisopropyl phosphoric ester, dibutyl phosphoric ester, di(2-ethylhexyl) phosphoric ester, diisodecyl phosphoric ester, etc.;
[0050] (V) As a boron complex, following - (V-1) (V-2) is mentioned.
The alcoholic hydroxyl-group-containing-compound complex of a boric acid; (V-1) A boric-acid ethylene glycol complex, boric-acid trimethylene-glycol complex, etc.;
The phosphoric acid and/or the phosphoric ester complex of a boric acid; (V-2) What is indicated to JP,2966451,B as a detail of; boron complexes, such as a boric-acid methyl phosphate complex and a boric-acid ethyl phosphate complex, can be used.
[0051] A carboxylic acid and an aromatic series sulfonic acid are [among these] desirable, it is a carboxylic acid and a sulfonic acid and they are a carboxylic acid and a polycyclic-aromatics sulfonic acid especially preferably still more preferably. These organic-acid anions may use a kind or two sorts or more.
[0052] Although not limited especially as the manufacture approach of ** (B), in the case of the 4th class ammonium organic-acid salt, tertiary amine is obtained with alkylating agents (alkyl halide, alkyl sulfuric acid, etc.) by making it react with an organic acid further after class[the / 4th]-izing, once changing halogen ion into the hydroxide ion, for example. The detail of this manufacturing method is indicated to the international disclosure patent WO 95/No. 15572, JP,2964244,B, etc., and can be manufactured by the same process.
[0053] The 3rd class sulfonium salt is obtained by making a sulfide react with an organic acid after class [the / 3rd]-izing with alkylating agents (alkyl halide, alkyl sulfuric acid, etc.), once changing halogen ion into the hydroxide ion further. the detail of this manufacturing method -- as a detail -- J.P.Marino,

"Topics in Sulfur Chemistry", and vol. -- it has indicated in 1, 1976, and p.1 grade, and can manufacture by the same process.

[0054] Moreover, the 4th class phosphonium salt is obtained by making the 3rd class phosphine react with an organic acid after class[the / 4th]-izing with alkylating agents (alkyl halide, alkyl sulfuric acid, etc.), once changing halogen ion into the hydroxide ion further. as the detail of this manufacturing method -- P.Beck"Organic Phosphorus Compound" and vol. -- it has indicated in 2, 1972, Chapt.4, and p.189 grade, and the same approach can be applied.

[0055] The 3rd class oxonium salt is obtained with alkylating agents (alkyl halide, alkyl sulfuric acid, etc.) in the ether by making it react with an organic acid further after class[the / 3rd]-izing, once changing halogen ion into the hydroxide ion. As a detail of this manufacturing method, it has indicated in G.W.Wheland, 1949, and p.38 grade, and the same approach can be applied.

[0056] Thus, in obtained ** (B), from withstand voltage and a heat-resistant viewpoint, the equivalent ratio of an onium cation and an organic-acid anion is onium cation:organic-acid anion =1:0.2-3 preferably, and is 1:0.5-1.5 still more preferably. Withstand voltage becomes it high that an organic-acid anion is 0.2 or more, and it excels in thermal resistance that it is three or less.

[0057] The electrolyte used for the electrolytic capacitor in this invention consists of (A) and (B). From a viewpoint of conductivity and withstand voltage, the weight ratio of ** (A) and ** (B) is (A):(B) =1:0.1-5 preferably, and is (A):(B) =1:0.2-2 still more preferably. Withstand voltage becomes it high that (B) is 0.1 or more, and conductivity is excellent in it being five or less. That is, from a viewpoint of withstand voltage, (** B) weight / ** (A) weight is 0.2 or more still more preferably, and is two or less still more preferably five or less preferably from a conductive viewpoint 0.1 or more.

[0058] In this invention, after this organic-acid onium salt (B) forms this conductive polymer (A), in case it may be introduced into a capacitor element and forms ** (A) by sinking in like the electrolytic capacitor using the conventional electrolytic solution, it may be introduced into a capacitor element by adding ** (B) at a polymerization and coincidence.

[0059] the electrolyte of this invention -- further -- a sparking-voltage improvement and formation -- additives various for the object, such as a sex improvement, leakage current reduction, hydrogen gas absorption, electrostatic-capacity change prevention, short prevention, corrosion prevention, a washability improvement, flameproofing, and an impregnating ability improvement, -- one or more sorts -- as it is -- or it can add in the form of a salt. as an additive -- phosphorus compounds (a phosphoric acid, phosphorous acid, and hypophosphorous acid --) boron compounds (a boric acid and boron oxide --), such as phosphoric ester and phosphonic acid A complex with the compound which has the ester of boric acid, boron, a hydroxyl group, and/or a carboxyl group etc., a nitro compound (a nitro benzoic acid, a nitrophenol, and a nitro phenetole --) sulfur compounds (sulfonic acids --), such as a nitro acetophenone and nitroaromatic benzoic-acid derivatives (a hydroxybenzoic acid --), such as a heterocyclic compound which has thiols and a sulfhydryl group phenols (a catechol --), such as a tetra-hydroxybenzoic acid and a benzoate oxy acid (a glycolic acid --), such as a nitro catechol and a trivalent phenol polyoxyethylenes, such as a tartaric acid and a citric acid, and/or a polyoxypropylene derivative (the polyoxyethylene nonylphenyl ether --) the compounds (mannite --) which have two or more hydroxyl groups, such as polyoxyethylene castor oil Hexit, Elislit, sorbitol, polyglycerin, a saccharide, and celluloses high molecular compounds (polyvinyl alcohol and a polyalkylene glycol --), such as starch A polyalkylene glycolic acid, polyacrylamide, a denaturation silicone oil, etc., A tungstic acid, heteropolyacids (a tungstosilicic acid, a tungstophosphoric acid, molybdophosphoric acid, etc.), particle inorganic compounds, such as a silicic acid anhydride, titanium oxide, and hydrotalcites, amino acid, etc. can be mentioned. From a conductive viewpoint, the amount of additives is 10 or less % of the weight of an electrolyte preferably, and is 5 or less % of the weight still more preferably.

[0060] Although the electrolyte of this invention may contain a solvent in the range which does not produce property degradation, it is desirable that it is a solid-state. as this solvent -- monoalcohol (a methanol, ethanol, and propanol --) glycols (ethylene glycol and a diethylene glycol --), such as isopropanol the mono-ether (methyl cellosolve --), such as triethylene glycol and tripropylene glycol Ethylcellosolve, methyl carbitol, ethyl carbitol, butyl carbitol, The triethylene glycol monomethyl ether,

the triethylene glycol monobutyl ether, Propylene glycol monomethyl ether, the propylene glycol monopropyl ether, Dipropylene glycol monomethyl ether, a tetrahydrofuran, etc., a diether (ethylene glycol wood ether and ethylene glycol diethylether --) Diethylene-glycol ethyl methyl ether, a jig lime, a TORIGU lime, Tetraethylene glycol wood ether, 1, 3-dioxane, etc., nitril (an acetonitrile, benzonitrile, etc.) and a ketone (an acetone --) Amides, such as a methyl ethyl ketone (dimethylformamide, dimethylacetamide, etc.), Carbonate (ethylene carbonate, propylene carbonate, etc.), ester (ethyl acetate, diethyl maleate, etc.) and lactone (gamma-butyrolactone --) Sulfur content solvents (dimethyl sulfoxide, sulfolane, etc.), halogenated hydrocarbon (chloroform, dichloromethane, etc.), and hydrocarbons (a hexane, toluene, etc.) are mentioned, and delta-valerolactones etc. are a glycol and lactone preferably. Two or more sorts of these solvents may be used. Ten or less % of the weight of an electrolyte is 5 or less % of the weight desirable still more preferably, and the amount of solvents is 1 or less % of the weight especially preferably. Moreover, in this electrolyte, moisture is 1% or less preferably, it is 0.3% or less still more preferably, corrosive-ion contents, such as alkali-metal ion and halogen ion, are 10 ppm or less preferably, and it is 1 ppm or less still more preferably. There is no electrolytic degradation that moisture is 1% or less, and there is no corrosion of an electrode that a corrosive-ion content is 10 ppm or less.

[0061] The electrolyte in this invention is used for an electrolytic capacitor component. The anode plate foil which consists of a valve action metal which was not limited especially as the above-mentioned electrolytic capacitor component, for example, formed the dielectric oxide film in the front face in the aluminium electrolytic condenser of a rolling-up form, You may be the capacitor element constituted by making a separator intervene and winding a cathode foil between them. The electrolyte which consists of a conductive polymer (A) and organic-acid onium salt (B) is prepared between an anode plate foil and a cathode foil. Said capacitor element for example After containing in a cylinder-like-object-with-base-like aluminum case, opening of an aluminum case can be sealed by the obturation agent, and an aluminium electrolytic capacitor can be constituted. It has an operation that the low electrolytic capacitor of the leakage current which has high withstand voltage can be obtained, by according to this electrolytic capacitor, being able to decrease resistance between poles remarkably in an electric conduction-ized part by using the high conductivity of a conductive polymer (A), combining the organic-acid onium salt (B) which has the restoration capacity of the dielectric oxide film of a valve action metal, and making it intervene at the same time the electrolytic capacitor which was excellent in the impedance characteristic as a result is obtained easily.

[0062]

[Example] Next, although the concrete example of this invention is explained, this invention is not limited to these.

[0063] The capacitor element was obtained by making a separator intervene between example 1 anode-plate aluminium foil and cathode aluminium foil, and winding around it. After being immersed for 10 minutes and pulling up this capacitor element at a room temperature in 5ml of water-ethanol (1:2) solutions containing ethylene dioxythiophene 0.5g and 2.0g of p-toluenesulfonic-acid iron, the process which carries out a desiccation polymerization at 105 degrees C for 10 minutes was repeated 10 times, and the capacitor element was rinsed - dried after forming the conductive quantity molecular layer which consists of chemistry polymerization polyethylene dioxythiophene between an electrode foil and an electrode foil (it is 10 minutes at 105 degrees C). Then, impregnation of phthalic acids 1, 2, and 3 and the 1g (equivalent ratio of the functional group of a phthalic acid / 3, and 4-tetramethyl imidazolinium salt = 1/1) of the 4-tetramethyl imidazolinium salt was carried out to this capacitor element, and the aluminum electrolysis capacitor element with rated voltage 50V electrostatic capacity of 220 micro F was obtained. [1, 2 and 3] After enclosing this capacitor element with the metal casing made from aluminum with an obturation member, opening was closed by curling processing and the aluminium electrolytic capacitor was constituted (size: phi10 mmxL10.2mm).

[0064] Examples 2-8 were performed like the example 1 except having used the conductive polymer or organic-acid onium salt which changes to the conductive polymer or organic-acid onium salt of an example 1, and has been indicated to a table 1.

[0065] The capacitor element was obtained by making a separator intervene between example of comparison 1 anode-plate aluminium foil, and cathode aluminium foil, and winding around it. Then, impregnation of the electrolytic solution 1 was carried out to this capacitor element, and the aluminum electrolysis capacitor element with rated voltage 50V electrostatic capacity of 220 micro F was obtained. After enclosing this capacitor element with the metal casing made from aluminum with an obturation member, opening was closed by curling processing and the aluminium electrolytic capacitor was constituted (size: phi13 mmxL10.2mm).
[0066] Electrolytic solution 1; 25% gamma-butyrolactone solution of phthalic acids 1, 2, and 3 and 4-tetramethyl imidazolinium salt.
[0067] In the example 1 of example of comparison 2 this invention, it was made to be the same as that of an example 1 except not sinking in organic-acid onium salt.
[0068] A table 2 compares the initial property [the electrostatic capacity in 120Hz, the impedance in 100kHz, a leakage current value, and the number of short generating (defect) under aging processing] about the aluminium electrolytic capacitor of the examples 1-8 of this invention, and the examples 1-2 of a comparison. The trial number is 50 pieces and all showed the initial property by the (the short article was removed) average.
[0069] An impedance is [aluminium electrolytic capacitor / which was constituted only using the electrolytic solution of the example 1 of a comparison / the examples 1-8 of this invention] remarkably larger than a table 2 a clear passage. In the example 2 of a comparison, since the restoration capacity of the oxide film of a good thing is remarkable and an impedance characteristic's is small, its short incidence rate under aging is high.
[0070]
[Effect of the Invention] The electrolytic capacitor using the electrolyte which consists of the conductive polymer (A) and organic-acid onium salt (B) by this invention does the following effectiveness so.
(1) (4) the leakage current excels [four] in (3) dependability which is excellent in few (2) impedance characteristics with high withstand voltage -- it can manufacture at an easy process.
[A table 1]

	導電性高分子	有機酸オニウム塩	
		酸	塩基
実施例2	ポリエチレンジオキシチオフェン	p－トルエンスルホン酸	1，2，3，4－テトラメチルイミダゾリニウム
実施例3	ポリエチレンジオキシチオフェン	フタル酸	1－メチル－3－エチルイミダゾリウム
実施例4	ポリエチレンジオキシチオフェン	p－トルエンスルホン酸	1－メチル－3－エチルイミダゾリウム
実施例5	ポリピロール	p－トルエンスルホン酸	1，2，3，4－テトラメチルイミダゾリニウム
実施例6	ポリピロール	フタル酸	1－メチル－3－エチルイミダゾリウム
実施例7	ポリエチレンジオキシチオフェン	ナフタレンスルホン酸	1－メチル－3－エチルイミダゾリウム
実施例8	ポリエチレンジオキシチオフェン	フェノール－4－スルホン酸	1－メチル－3－エチルイミダゾリウム

[A table 2]

	静電容量 (μF at 120Hz)	インピーダンス (mΩ at 100kHz)	漏れ電流 (μA)	ショート発生数 (個)
実施例1	221	28	13	0
実施例2	219	24	17	0
実施例3	222	23	14	0
実施例4	225	25	13	0
実施例5	223	26	15	0
実施例6	221	25	16	0
実施例7	225	23	13	0
実施例8	220	24	16	0
比較例1	218	145	12	0
比較例2	207	22	152	23

[Translation done.]